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(54) PHOTO RESIST COMPOSITION AND PROCESS

(71) We, NORLAND PRODUCTS INC., a corporation organised and existing under the laws of the State of New Jersey, United States of America, of 695 Joyce Kilner Avenue, New Brunswick, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to protein-based photo resists.

One of the newer ways of forming precisely defined thin metal parts is by photo chemical machining, sometimes referred to as photo fabrication or chemical milling. To do this a photo sensitive coating, hereinafter referred to as a photoresist, is applied to both sides of a thin metal sheet. The metal sheet with the photo resist coating is then placed between a sandwich of exactly registered negatives, and then exposed to a high intensity ultra violet light source. Where the light penetrates the clear areas of the negative, the photo resist is changed. In the case of a negative working photo resist, the light will insolubilize the coating. The metal sheet is then washed in an appropriate solvent, which dissolves away the unexposed and still soluble areas, leaving an image on the metal. After drying and baking, this image now acts as an acid resist to prevent corrosive acid substances from attacking the underlying metal. The metal sheet is placed in an etcher, where acid is impinged against the sheet and etches away the part not protected by the acid resist. This method has several advantages over the die stamping method of making thin metal parts. For instance, closer tolerance can be maintained, no burrs are obtained as in die stamping, and the metal is not stressed. It is possible to make parts more quickly as considerable time is required to make a proper metal die. Where a small number of parts are required, photo chemical machining is cheaper than die stamping, as the negatives required are much cheaper to make than a metal die, which requires an experienced craftsman. However, there are definite limitations to photo chemical machining. Where large numbers of parts are required, and where the other requirements are not as stringent, die stamping is lower in cost.

Recent developments in photo chemical reactions have resulted in a great number of various photo resists being commercially available. In spite of this, the rate of growth of parts made by photo chemical machining has not concomitantly increased. Part of this is due to the fact that designers and engineers are not fully acquainted with this technique of making sheet metal parts, and hence photo chemical machined parts are not designed into new equipment.

Another disadvantage is that in some cases the process has not moved out of the exotic class to reach the scale of widespread industrial applications. There are small manufacturers of photo chemical machined parts who process single sheets that range in size up to one square foot and rarely as large as two square feet. The type of photo resist coating compositions used by these relatively small manufacturers are generally quite expensive, ranging in price from \$30 to \$100 per gallon. Although in practice the coating thickness is very thin, of the order of 0.05—1.0 mil, the cost is multiplied as special equipment to handle flammable organic solvents is required, and the special developing solvents and stripping solutions that are required are very costly. The net result is the small manufacturer develops a pricing structure that takes into account the single sheet operation, the high cost of photo resist coating compositions and resultant processing fluids. For a manufacturer interested in a potential high volume part the cost can become uneconomical.

The problem of handling solvents and special phenolic containing solvent stripping solutions is well known to the trade, and some photo resist manufacturers have developed products that require water-based caustic solutions to wash out the image, or afterwards dissolve the image. These still

suffer from the same disadvantages in that they require solvents in the photo resist and the photo resist itself is considered to be relatively expensive.

The use of this technique of making thin metal parts by a chemical etching process was developed from the photo-engraving trade. In making a letterpress printing plate, an image is applied to a metal plate using the photo resist technique. The plate is then etched with acid to give a raised letterpress plate. One of the original photo resists was based on a mixture of fish glue, ammonium bichromate, and water. This evolved into a specially refined fish glue, a clear liquid somewhat like dark honey in color and vicosity, and called photoengravers glue. Because of the nature of the companies manufacturing this product, photoengraving glue was of the right quality, it adhesive than a photographic base. As a result, the product did have inconsistencies and its faults were attributed to the product rather than the manufacturer. When photoengraving glue was of the right quality, it was generally agreed that the product worked very well.

In the last 10 years, the manufacturing process for making photoengraving glue has improved to the point where it is very consistent, and can be used with good dependability, thus it has considerable advantage. These materials have been applied as photo resists in photo chemical machining. The cost of a gallon of photo resist made from photoengraving glue, ammonium bichromate and water can be as low at $4 per gallon and is a water solution that does not require special venting or explosion proof equipment as with organic solvent based photo resists. Water is used for removing the still soluble areas of the coated part after exposure, known in the art as "developing" and a 10% solution of caustic in water will strip the photo resist after etching.

The use of photoengraving glue is of special interest to manufacturers who are set up to make metal parts by a continuous chemical machining process. In this known process a roll of metal is unwound and run through a washing process to clean the metal. The wet metal is then flow coated with the water based photo-engraving glue resist and dried. The coated metal is run through printing chases where glass negatives are drawn up tight against the metal and the image exposed by an intense source of ultra-violet light. The sheet is then run through a water wash to develop the image, dried, and baked at a 500—550°F. temperature. Next the sheet passes through etchers which spray hot ferric chloride solution against the metal to etch out the open areas. Following this the resist is removed with a hot caustic solution All of this can be in one continuous process, or it can be broken into two or three steps. Since a continuous web is processed, favourable economies are achieved. This process is described in U.S. Patent 2,762,149 and in the February 8, 1971 issue of *American Machinist.* The largest volume production is the aperture mask or shadow mask which is a part of every color TV tube. To show the acceptance of photoengraving glue, all aperture mask manufacturers in the United States are using it in their continuous process. This is because the total cost of photoengraving glue photoresist, water for veloping, and 10% caustic in water stripper, is very nominal and can represent a tremendous saving compared to the cost of the chemicals used in solvent based resists. Another advantage is in the ease of handling water based solutions, compared to solvent based solutions especially in large volume manufacturing operations.

In spite of the low cost and processing advantages, there are limitations which curtail the use of photo-engraving glue as a photoresist. The bake-in or curing temperature of 500°—550°F. for up to 5 minutes is critical. Too high a temperature for too long a time will result in embrittlement and resist failure and too low a temperature results in insufficient acid resistance. Although a 48° Baumé ferric chloride is generally used, a lower Baumé will give faster etching. As the Baumé is reduced, there is more chance for resist failure. Pinholding also represents a problem, as heavier metals require longer etch time with resultant longer exposure of the photo resist to the etchant. A pinhole will result in an imperfect part, as the etchant penetrates the photo resist where the metal should be protected. Six mils metal generally can be etched satisfactorily with a normal 0.1 to 0.3 mil coating of photoengraving glue resist. For heavier metals up to 10 mils, a heavier coating up to 0.4 mil is required. Over 10 mils metal is processed only under special care and conditions. Another problem is the normal photoengraving glue-bichromate photo resist cannot stand cycling between ferric chloride etchant and water. In single sheet operation the metal is etched, washed with water, and inspected to determine if dimensional tolerances are met. If not the part is put through the etching cycle again. Although this type of failure is true with all photo resists, it is especially a fault of a photoengraving bluebichromate resist at the present state of the art. The photo resist will soften during the second etching cycle, and slough off leaving the entire metal exposed to the etchant. In continuous chemical machining this is not the same problem as the sheet is not recycled through the etchant.

As can be readily seen, the adoption of large volume production of photochemically

machined thin metal parts is dependent upon the economies of the process and the material costs. The use of water-based photoengraving glue allows for a simplified manufacturing operation, as solvents do not have to be vented nor do waste solvents have to be disposed of. The cost of the expendable materials—photo resist, developer, and stripper—is very low with a continuous process and the producer can maintain optimum economies using a photoengraving glue photo resist.

The present invention provides a method of improving the acid resistance of protein-based photo resists, and especially photoengraving glue photo resists which are used by large volume continuous photo chemical machining procedures. By means of the material and process disclosed herein, improvements are obtained in acid resistance which extend the potential use of protein-based photo resists in photo chemical machining. The temperature of post-bake or cure is reduced, and is no longer as critical thereby reducing serious damage to the metal part through operator error. The photo resist will withstand a lower Baumé ferric chloride for longer periods of time without failure hence decreasing the etching time required, and the acid resistance after cycling between ferric chloride and water is greatly increased. Pinholding is greatly reduced, and thinner photo resist layers withstand the acid etch for a longer period of time. With heavier photo resist coating, metals thicker than 10 mils can be etched without special care and handling, thus greatly expanding the industrial potential of photo chemical maching.

In addition to the aforementioned advantage of improved resistance to etch solutions, an additional advantage is the improvement in the "overhang" of the resist during etching. "Overhang" is the resist that remains suspended after part of the metal underneath has been dissolved. Normally the overhang may tend to become misshapen by chipping of edges (too brittle) or sagging (too soft). This effect may be exaggerated when the metal part is returned to the etch bath one or more times. Overhangs produced by this invention are smooth and straight, showing no chipping or sagging.

In addition to the above advantages, another advantage is shown in stripping (removal of the resist after the etching step). Resists produced by this invention can be stripped from the metal in a shorter time than resists not utilizing one of the acids used in the process of this invention. This translates into economic savings by reducing the time required to carry out the stripping.

A further advantage of this invention is that lower bake temperatures can be used. Normally a temperature of 500—550°F. is required. This invention allows the production of effective resists down to a 200°F. bake temperature which results in greater flexibility of operations and reduces the number of rejected parts. Examples will show this effect.

A still further advantage of this invention is the reduction in the pinholing which results in greater productivity by reducing the percentage of rejects.

The present invention provides means for markedly improving the etch resistance of the protein-based resist.

In its first aspect the invention provides a photo-resist composition comprising an aqueous solution of protein material of natural origin and an organic acid modifying agent selected from cycloaliphatic polycarboxylic acids, heterocyclic polycarboxylic acids, aromatic polycarboxylic acids and aromatic suphonic acids, which aromatic sulphonic acids are free from substituents except alkyl groups, and a photosensitive material that on exposure to ultra-violet light, renders the composition substantially insoluble in water.

In its second aspect the invention provides a process for the photo-chemical machining of a thin metal article which process comprises

(a) exposing both surfaces of a thin metal article, having a coating on both sides thereof of a composition obtained by drying a composition as described above, to a source of ultra-violet light through a pair of negatives in exact register, the first negative on the first side of the coated metal article, the second negative on the second side of the coated metal article, thereby rendering the exposed portions of the coating insoluble in water and leaving the unexposed portions of the coating substantially water soluble;

(b) washing the exposed metal article with water thereby dissolving the unexposed portions of the photo-resist coating, and allowing the washed metal part to dry;

(c) heating the washed metal article at a temperature sufficient to cure the photo-resist coating remaining thereon; and

(d) etching the metal article with a corrosive inorganic acid thereby removing the remaining uncoated partions of the metal article leaving the coated portions and underlying metal.

In its third aspect the invention provides a process for the photo-chemical machining of a thin metal article which comprises the steps of:

(a) applying to both surfaces of the thin metal article a photo-resist coating

comprising a protein material of natural origin and a photo-sensitive material that, on exposure to ultra- violet light, renders the coating substantially insoluble to water, and drying the photo-resist coating;

(b) exposing both surfaces of the coated metal article to a source of ultra-violet light through a pair of negatives in exact register, the first negative on the first side of the coated metal, the second negative on the second side of the coated metal article, thereby rendering the exposed portions of the coating insoluble in water and leaving the unexposed portions of the coating substantially water soluble;

(c) washing the exposed metal article with water thereby dissolving the unexposed portions of the photo-resist coating, and allowing the washed metal part to dry;

(b) treating the exposed portions of the photo-resist with an organic acid modifying agent selected from cycloaliphatic polycarboxylic acids, heterocyclic polycarboxylic acids, aromatic polycarboxylic acids and aromatic sulphonic acids, which aromatic sulphonic acids are free from substituents containing nitrogen atoms, thereby improving the acid resistance of the protein-based photo-resist;

(e) heating the metal article at a temperature sufficient to cure the photo-resist coating remaining thereon; and

(f) etching the metal article with a corrositive inorganic acid thereby removing the remaining uncoated portions of the metal article leaving the coated portions and underlying metal.

Although we do not wish to be bound by any particular theories, it is believed that the protein reacts with the organic acid modifier to improve the acid resistance properties of the resist. Mixtures of the above organic acid modifiers may be used.

As the protein-based material there may be used the polypeptide material derived from collagen such as fish glue, animal glue, gelatin, as well as casein and albumin all being derived from natural sources. These materials are already well known in the art and are described in Kirk-Othmer, Encyclopaedia of Chemical Technology (second Edition) Volume 10, pages 604—618. The preferred protein materials are fish glues derived from fish collagen.

Conventional photo sensitizers are included in the composition of the photoresist. These materials are commonly known in the art and a list of photo sensitizers are given in Kosar, "Light Sensitive Systems", John Wiley & Sons, New York, N.Y., pages 52 and 160 to 187. Those skilled in the art will have not difficulty, having regard to their own knowledge and the disclosure herein, in identifying photo sensitizers suitable for use in the present invention. Ammonium bichromate is the preferred sensitizer.

It is also necessary to include a substantial quantity of water in the formulation, first to dilute the rather substantial amount of glue, then to dissolve the other ingredients.

The organic acid modifier usually present in an amount of at least 0.01%, usually 0.01 to 25%, based on the weight of the dry protein, although concentrations as high as the solubility of the acid in the aqueous protein solution can be used. For the sake of economy and correct practice, an amount of 1 to 25 weight percent is preferred. The acid may be incorporated in the aqueous protein solution or incorporated by dipping a light-hardened protein coated plate into a solution of the acid. As examples of cycloaliphatic polycarboxylic acids having 3 to 7, preferably 4 to 6, carbon atoms in the cyclic ring there may be cyclobutane, cyclopentane or cylohexane and derivatives thereof containing two or more carboxyl groups. Preferred are cycloalkane polycarboxylic acids having 4 to 6 carbon atoms in the cycloalkane and having 2 to 4 carboxylic acid groups. Examples are 1,1-cyclobutane dicarboxylic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, 1,2-cyclohexane dicarboxylic acid and 1,2,3,4-cycloheptane tetracarboxylic acid.

The heterocyclic polycarboxylic acids may be derivatives of a heterocyclic compound such as pyridine, piperazine, tetrahydrofuran and thiophene such as 2,6-pyridine dicarboxylic acid, 3,5-pyridine dicarboxylic acid, 2,6-piperazine dicarboxylic acid, 3,5-piperazine dicarboxylic acid, 2,6-thiophene dicarboxylic acid, 3,4-tetrahydrofuran dicarboxylic acid and 2,5-tetrahydrofuran dicarboxylic acid.

The aromatic polycarboxylic acids are those having carboxyl groups attached to an aromatic ring; of course more than one aromatic ring may be present, such as those acids based on naphthalene, benzophenone and diphenylmethane nuclei. Among the acids we have found to be particularly effective are 1,2,4,5-benzene tetracarboxylic acid (pyromellitic acid), 3,4,3[1],4[1]-benzophenone tetracarboxylic acid (BPTA); 1,2,4-benzene tricarboxylic acid (trimellitic acid); 1,2,3,4,5,6-benzene hexacarboxylic acid (mellitic acid) and 1,2,3-benzene tricarboxylic acid (hemimellitic acid). The most preferred aromatic acids according to the present invention are trimellitic and pyromellitic.

The aromatic sulfonic acids that are useful include p-toluene sulfonic acid, 2-naphthalene sulfonic acid, naphthalene 1,8-disulfonic acid, benzene sulfonic acid and 1,3-benzene disulfonic acid.

Other useful acids will be those having

certain substituted groups on the aromatic ring. For example, any one or all of the three remaining hydrogens on trimellitic acid can be substituted with a lower alkyl group having up to 6 carbon atoms or a halogen such as fluorine, chlorine or bromine with the resulting acid still being an effective reactant in producing a more resistant resist. When the acidic materials are mixed with a coating composition a preferred formulation according to the invention contains about 10 to 15 parts of dry protein-based glue 0.5 to 5 parts photo sensitizer, 0.1 to 5 parts of acidic material and a sufficient quantity of water to dissolve the glue and achieve the desired viscosity.

In carrying out the processes of the invention, the washing of the unexposed, soluble photo resist coated metal is suitably carried out by means of a room temperature water wash, and the metal piece is suitably etched with ferric chloride in the known manner. In the processes constituting the third aspect of the invention, the modifying organic acid is not included in the photosensitive glue coating, but is later applied to the developed metal piece as a separate step, preferably as an aqueous solution. The amount of acidic modifying material applied varies with the operational conditions but at least 0.01 weight percent is generally present, preferably at least 0.125% weight percent, especially at least 0.25 weight percent and particularly an amount of from 1 to 25 weight percent of the solution in which it is applied is used. The temperature at which the organic acid modifier is applied is not critical; for convenience ambient temperatures are used. It will be appreciated that only minor modifications are necessary in existing photo resist chemical machining operations to include the organic acid modification step as herein described. As will be appreciated, the organic acid modifier may be applied as a dip, spray or other means generally known in the art.

As the ultra-violet light source there is used arc lamps, pulsed Xenon lamps and mercury vapor lamps, although any source of ultra-violet light can be used. A typical photo exposure can be carried out using Model DMVL Exposure Unit, manufactured by Colight, Inc., Minneapolis, Minn. 55401, using an exposure time from 2 to 4 minutes.

It will be appreciated that normal etching time varies with several factors including type and thickness of the metal, the type and concentration of the etchant and temperature of the etchant.

The following examples are representative of embodiments of the present invention which is not limited thereto. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1:

In a test for surface failure, two stainless steel plates 5 mils thick were both coated in a whirler coater using a solution containing the following ingredients in parts by weight:

	parts
Fish glue water solution (45% solids)	50
ammonium bichromate	5
water	125

The dried coating on the plates was approximately 0.2 mil thick. The coated plates were then exposed to ultra-violet light in the equipment previously described for 4 minutes, after which they were washed with room temperature tap water for 1 minute. Plate 1, while still wet, was dipped in a 1% solution of trimellitic acid for 15 seconds, rinsed under the tap for 2 seconds and dried. Another coated plate, plate A, was treated similarly, with the exception it was not dipped in the trimellitic acid solution and therefore served as a control. The plates were then heated at 525° F. for 10 minutes after which they were subjected to an etch solution (40° Be $FeCl_3$) spray at 120° F. until they failed; failure was indicated when there was an obvious break in the resist coating. The plates were visually inspected at 5 minute intervals with the following results observed, the time to failure being the elapsed time from initiation of the application of the etch solution to an obvious break in the resist coating.

Plates		Time to Failure
1	(Dipped in trimellitic acid solution)	Greater than 105 minutes
A	(control)	25 minutes

Although in the preparation of the resist, as indicated above, a 2 second water rinse was used, it has been found that this step is not necessary. An improved procedure is to omit the rinse step after dipping in the acid solution and then dry immediately by air jet. It is believed this procedure eliminated any residual acid that may have been deposited on the exposed metal surface.

EXAMPLE 2:

A stainless steel plate 5 mils thick was coated in the same manner as Example 1

with the following solution in a whirler coater:

Formulation I

	parts
Fish glue water solution (45% solids)	50
ammonium bichromate	5
water	125

The plate coated with Formulation I was designated as the control and was labeled B.

A second stainless steel plate also 5 mils thick was coated in the same manner with a solution similar to the B plate coating but including pyromellitic acid. The following solution was applied in a whirler coater:

Formulation II

	parts
Fish glue water solution (45% solids)	50
ammonium bichromate	5
water	125
pyromellitic acid	0.23

The plate coated with Formulation II was labeled 2.

The plates were heated at 525° F. for 10 minutes. Both plates were then subjected to an etch solution as described in Example 1 with the following results:

Plates	Time to Failure
B (control)	25 minutes
2	85 minutes

EXAMPLES 3 to 13:

Following the procedure and the base composition of Example 1 in which the control failed in 25 minutes, the effectiveness of various other polycarboxylic acids are as follows:

Example	Acid (% solution in water, approximate)	Time to Failure
3	pyromellitic acid (1%)	85 minutes
4	trimesic acid (0.5%)	over 65 minutes
5	phthalic acid (<0.5%)*	40 minutes
6	hemimellitic acid (2%)	70 minutes
7	mellitic acid (2%)	60 minutes
8	pyridine 2,6-dicarboxylic acid* (<0.5%)	70 minutes
9	p-Toluenesulfonic acid (2%)	80 minutes
10	1,2,3,4-cyclepentane tetracarboxylic acid (5%)	80 minutes
11	2-Naphthalene sulfonic acid (16%)	75 minutes
12	Vanderbilt's PD230** (1%)	75 minutes
13	1,3-Benzene disulfonic acid (16%)	50 minutes
14	Benzene pentacarboxylic acid (2%)	over 75 minutes

* acid is poorly soluble in water

** 4,4[1]-(2-acetoxy-1,3-glyceryl)bis-anhydro trimellitate

COMPARATIVE EXAMPLES C—F

Using the same procedure and base composition as in Example 1, in which the control failed in 25 minutes, other types of acids were found to be relatively ineffective as shown by the following examples; the listed acids being used in place of trimellitic acid:

Example	Acid (% solution in water, approximate)	Time to Failure
C	ethane sulfonic acid (8%)	10 minutes
D	maleic acid (10%)	25 minutes
E	dodecenyl succinic acid (1%)	25 minutes
F	copolymer of methyl vinyl ether and maleic acid derived from GAF Gantrez 119*, (5%) ("Gantrez" is a Registered Trade Mark)	25 minutes

* This is commercially available as GANTREZ 119 sold by the GAF Corporation, New York, N.Y.

EXAMPLE 15

Following the procedure and the base composition of Example 1 except using lower bake temperatures, the following data indicate the effectiveness of the lower bake temperature:

Brake Temperature	Treated With Trimellitic Acid Solution	Time to Failure
350°F.	Yes	Greater than 75 minutes
350°F. (Control)	No	30
250°F.	Yes	Greater than 75 minutes
250°F. (Control)	No	5

EXAMPLE 16:

Following the procedure of Example 1 but substituting a borax-caseinate for fish glue and using a bake temperature of 400°F., the following results were obtained:

Treated With Trimellitic Acid Solution	Time to Failure
Yes	Greater than 65 minutes
No (Control)	35 minutes

EXAMPLE 17:

Following the procedure of Example 1 except using a highly hydrolysed lime-gelatin in place of fish glue and using a bake temperature of 400°F., the following results were obtained:

Treated With Trimellitic Acid Solution	Time to Failure
Yes	50 minutes
No (Control)	35 minutes

EXAMPLE 18:

Following the procedure of Example 1 except using a bake temperature of 200°F. and varying the concentration of the trimellitic acid solution, the following results were obtained:

Conc. of Trimellitic Acid Solution	Time to Failure
2.0%	40 minutes
1.0%	40 minutes
0.5%	30 minutes
0.25%	30 minutes
0.125%	20 minutes
0.0%	10 minutes

This shows very clearly that the concentration of the dip solution is important in obtaining the desired etch resistance.

EXAMPLE 19:

Following the procedure of Example 1, except using a bake temperature of 300°F. and varying the time of dip, the following results were obtained:

Time of Dip In The Trimellitic Acid Solution	Time to Failure
15 seconds	Greater than 75 minutes
5 seconds	70 minutes
0 seconds (Control)	10 minutes

This shows that the time of dip is important in obtaining the desired etch resistance.

WHAT WE CLAIM IS:—

1. A photoresist composition comprising an aqueous solution of protein material of natural origin and an organic acid modifying agent selected from cycloaliphatic polycarboxylic acids, heterocyclic polycarboxylic acids, aromatic polycarboxylic acids and aromatic sulfonic acids, which aromatic sulphonic acids are free from substituents except alkyl groups, and a photosensitive material that on exposure to ultra-violet light, renders the composition substantially insoluble in water.

2. A composition according to claim 1 wherein the organic acid modifying agent is present in an amount of 0.01 to 25.0 weight percent based on the protein material.

3. A composition according to claim 2 wherein the organic acid modifying agent is present in an amount 1 to 25 weight percent based on the protein material.

4. A composition according to claim 1, 2 or 3 wherein the protein material is fish glue.

5. A composition according to claim 1, 2 or 3 wherein the protein material is animal glue, gelatin, casein or albumen.

6. A composition according to any one of the preceding claims wherein the organic acid modifying agent is a cycloalkane polycarboxylic acid having 3 to 7 carbon atoms in the cycloalkane and 2—4 carboxyl groups.

7. A composition according to claim 6 wherein the cycloalkane polycarboxylic acid is selected from 1,1-cyclobutane dicarboxylic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, 1,2-cyclohexane dicarboxylic acid and 1,2,3,4-cycloheptane tetracarboxylic acid.

8. A composition according to any one of claims 1 to 5 wherein the organic acid modifying agent is a heterocyclic poly carboxylic acid which is a derivative of pyridine, piperazine, tetrahydrofuran or thiophene having from 2—4 carboxyl groups.

9. A composition according to claim 8 wherein the heterocyclic polycarboxylic acid is selected from 2,6-pyridine dicarboxylic acid, 3,5-pyridine dicarboxylic acid, 2,6-piperazine dicarboxylic acid, 3,5-piperazine dicarboxylic acid, 2,6-thiophene dicarboxylic acid and 3,4-tetrahydrofuran dicarboxylic acid.

10. A composition according to any one of claims 1 to 5 wherein the organic acid modifying agent is an aromatic polycarboxylic acid which contains from 6 to 14 carbon atoms and has from 2 to 7 carboxyl groups attached to the aromatic ring.

11. A composition according to claim 10 wherein the aromatic polycarboxylic acid is selected from pyromellitic acid, trimellitic acid, mellitic acid, hemimellitic acid and 3,4,3[1],4[1]-benzophenone tetracarboxylic acid.

12. A composition according to claim 4 wherein the protein material is fish glue and the organic acid modifying agent is trimellitic acid.

13. A composition according to any one of the preceding claims which contains 10 to 15 parts by weight of the protein material, 0.5 to 5 parts by weight of the photosensitiser and 0.1 to 5 parts by weight of the organic acid modifying agent.

14. A composition according to claim 1 substantially as hereinbefore described.

15. A process for preparing a composition as claimed in any one of the preceding claims which comprises adding the organic acid modifying agent and the photosensitive material to an aqueous solution of the protein material.

16. A thin metal article having a coating on both surfaces thereof of a composition obtained by drying a composition as claimed in any one of claims 1 to 14.

17. A process for the photo-chemical machining of a thin metal article which comprises the steps of:

(a) applying to both surfaces of the thin metal article a photo-resist coating comprising a protein material of natural origin and a photo-sensitive material that, on exposure to ultra- violet light, renders the coating substantially insoluble to water, and drying the photo-resist coating;

(b) exposing both surfaces of the coated metal article to a source of ultra-violet light through a pair of negatives in exact register, the first negative on the first side of the coated metal, the second negative on the second side of the coated metal article, thereby rendering the exposed portions of the coating insoluble in water and leaving the unexposed portions of the coating substantially water soluble;

(c) washing the exposed metal article with water thereby dissolving the unexposed portions of the photo-resist coating, and allowing the washed metal part to dry;

(d) treating the exposed portions of the photo-resist with an organic acid modifying agent selected from cycloaliphatic polycarboxylic acids, heterocyclic polycarboxylic acids, aromatic polycarbwhich aromatic sulphonic acids are free oxylic acids and aromatic sulfonic acids, from substituents except alkyl groups, thereby improving the acid resistance of the protein-based photo-resist;

(e) heating the metal article at a temperature sufficient to cure the photo-resist coating remaining thereon; and

(f) etching the metal article with a corrosive inorganic acid thereby removing the remaining uncoated portions of

the metal article leaving the coated portions and underlying metal.

18. A process according to claim 17 wherein the protein material is fish glue.

19. A process according to claim 17 wherein the protein material is animal glue, gelatin, casein or albumen.

20. A process according to claim 17, 18 or 19 wherein the organic acid modifying agent is as defined in claim 6 or 7.

21. A process according to claim 17, 18 or 19 wherein the organic acid modifying agent is as defined in claim 8 or 9.

22. A process according to claim 17, 18 or 19 wherein the organic acid modifying agent is as defined in claim 10 or 11.

23. A process according to claim 18 wherein the organic acid modifying agent is trimellitic acid.

24. A process according to any one of claims 17 to 23 wherein the organic acid modifying agent is applied to the exposed portions of the photo-resist in the form of an aqueous solution containing 1 to 25% by weight of the organic acid.

25. A process according to claim 17 substantially as described in any one of the foregoing Examples.

26. A photo-chemically machined metal article produced by a process as claimed in any one of claims 17 to 25.

27. A process for the photo-chemical machining of a thin metal article which comprises:

(a) exposing both surfaces of a thin metal sheet as claimed in claim 16 to a source of ultra-violet light through a pair of negatives in exact register, the first negative on the first side of the coated metal article, the second negative on the second side of the coated metal article, thereby rendering the exposed portions of the coating insoluble in water and leaving the unexposed portions of the coating substantially water soluble;

(b) washing the exposed metal article with water thereby dissolving the unexposed portions of the photo-resist coating, and allowing the washed metal part to dry;

(c) heating the washed metal article at a temperature sufficient to cure the photo-resist coating remaining thereon; and

(d) etching the metal article with a corrosive inorganic acid thereby removing the remaining uncoated portions of the metal article leaving the coated portions and underlying metal.

28. A process according to claim 27 substantially as hereinbefore described.

29. A photo-chemically machined metal article produced by a process as claimed in claim 27 or 28.

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